Programme: Bachelor of Science (Third Year)

Subject : Chemistry

Semester : V

Course code: CHC 106

Course Title: Inorganic chemistry (Section A)

Title of the Unit: Unit-1 :Inorganic Solid State Chemistry

Module Name: Metal excess defects and Metal deficiency defects

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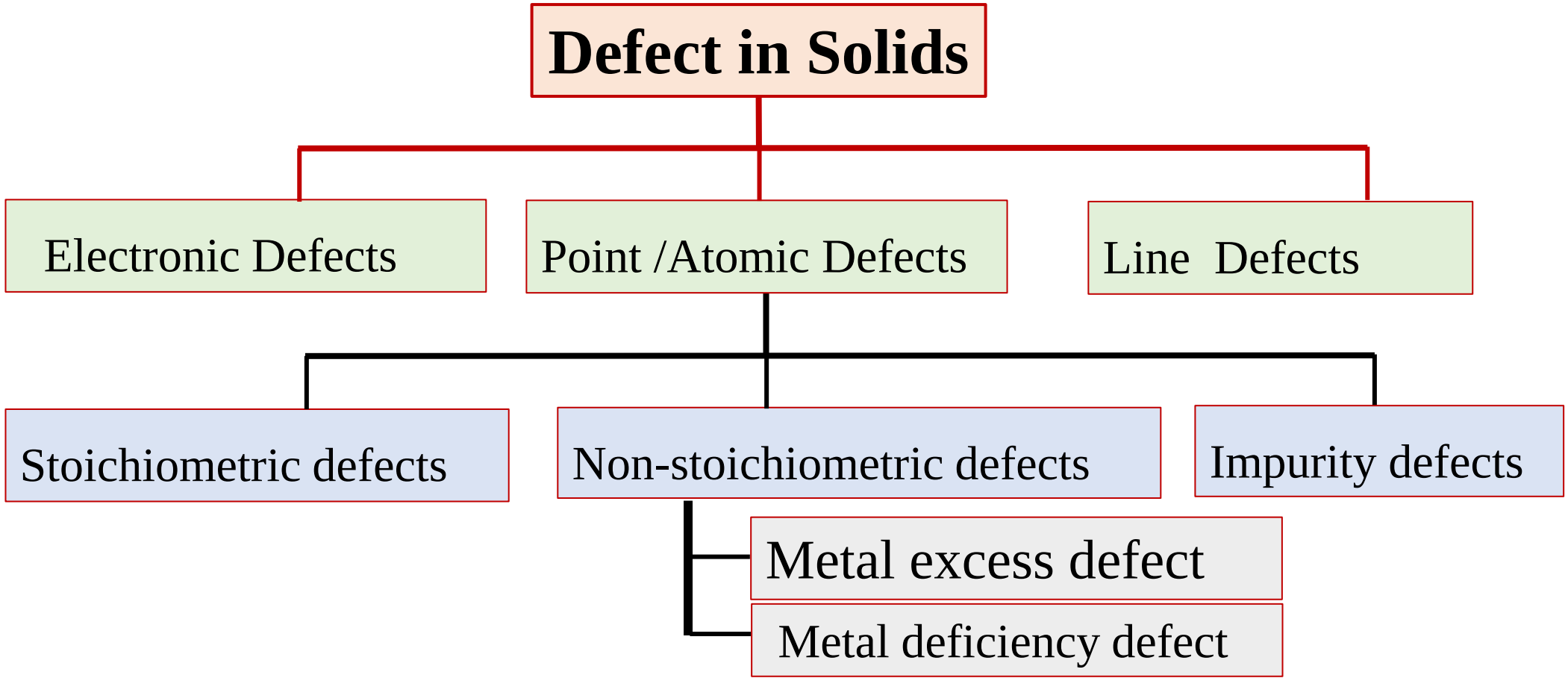
OUTLINE

- Defects in solids
- Non-stoichiometric defects
- Metal excess defects
- Metal deficiency defects

LEARNING OUTCOMES

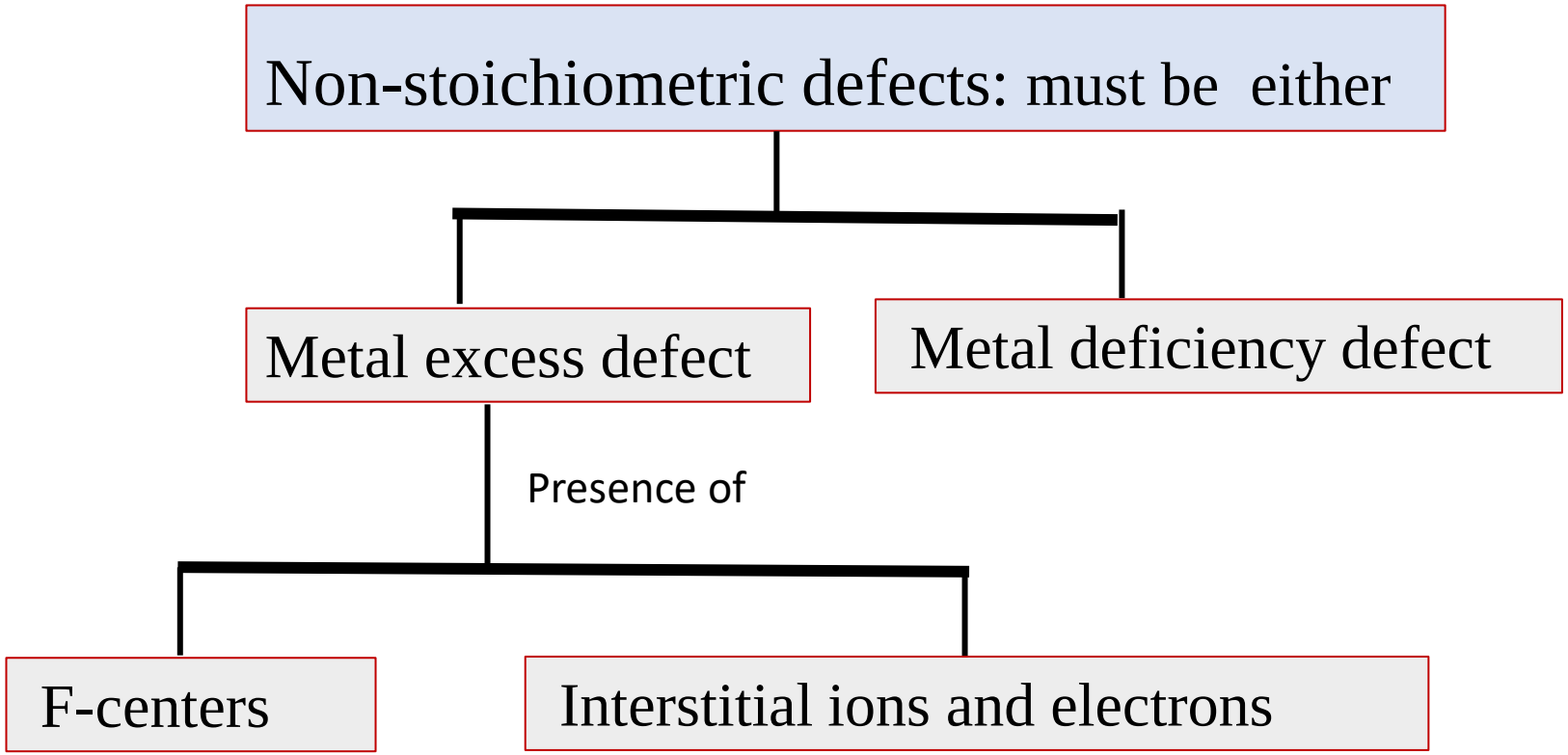
At the end of this module students will be able to:

- List down defect in solids
- Explain point defects
- Differentiate between stoichiometric and Non stoichiometric defects
- Compare metal excess and metal deficiency defects


Defect in Solids
Electronic Defects
Point /Atomic Defects
Line Defects
Stoichiometric defects
Non-stoichiometric defects
Impurity defects
Metal excess defect
Metal deficiency defect

Non -stoichiometric (Berthollide) defects:

- Exist in compounds in which numbers of cations and anions are different from that indicated in the ideal chemical formula. (E.g. In $Fe_{0.84}O$, the ratio of Fe:O ≠1:1).
- Compounds must have either cations or anions in excess, compounds do not obey the law of constant composition.
- However electrical neutrality of a solid is maintained either by having extra electrons in the structure or changing the charge on some of the metal ions. This makes the structure irregular, i.e. it contains defects.

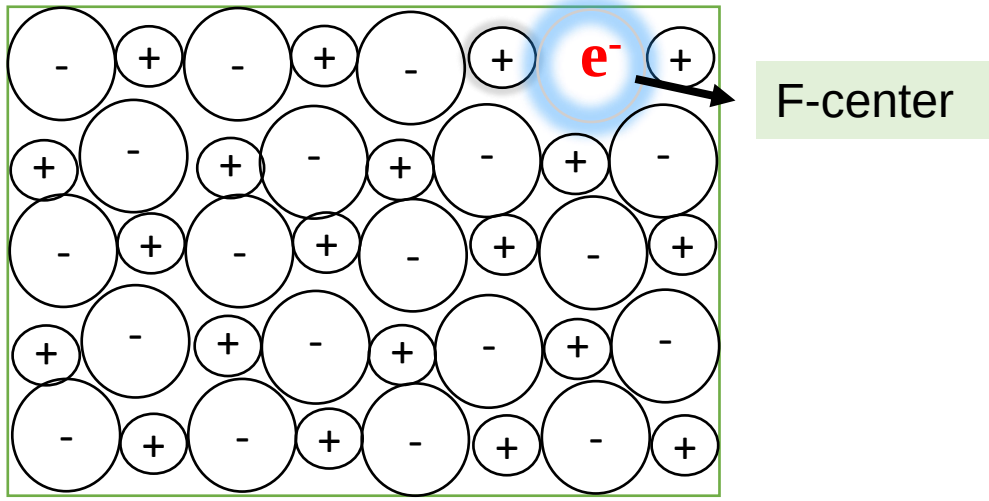

Non-stoichiometric defects: must be either
Metal excess defect
Metal deficiency defect
Presence of
F-centers
Interstitial ions and electrons

Metal excess defects :In these defects the positive ions are in excess due to:

1. **Anionic vacancy** (F–centers): Anions may be missing from its lattice sites leaving a hole which are occupied by an extra unpaired electron to maintain the electrical neutrality of the solid (F–centers).

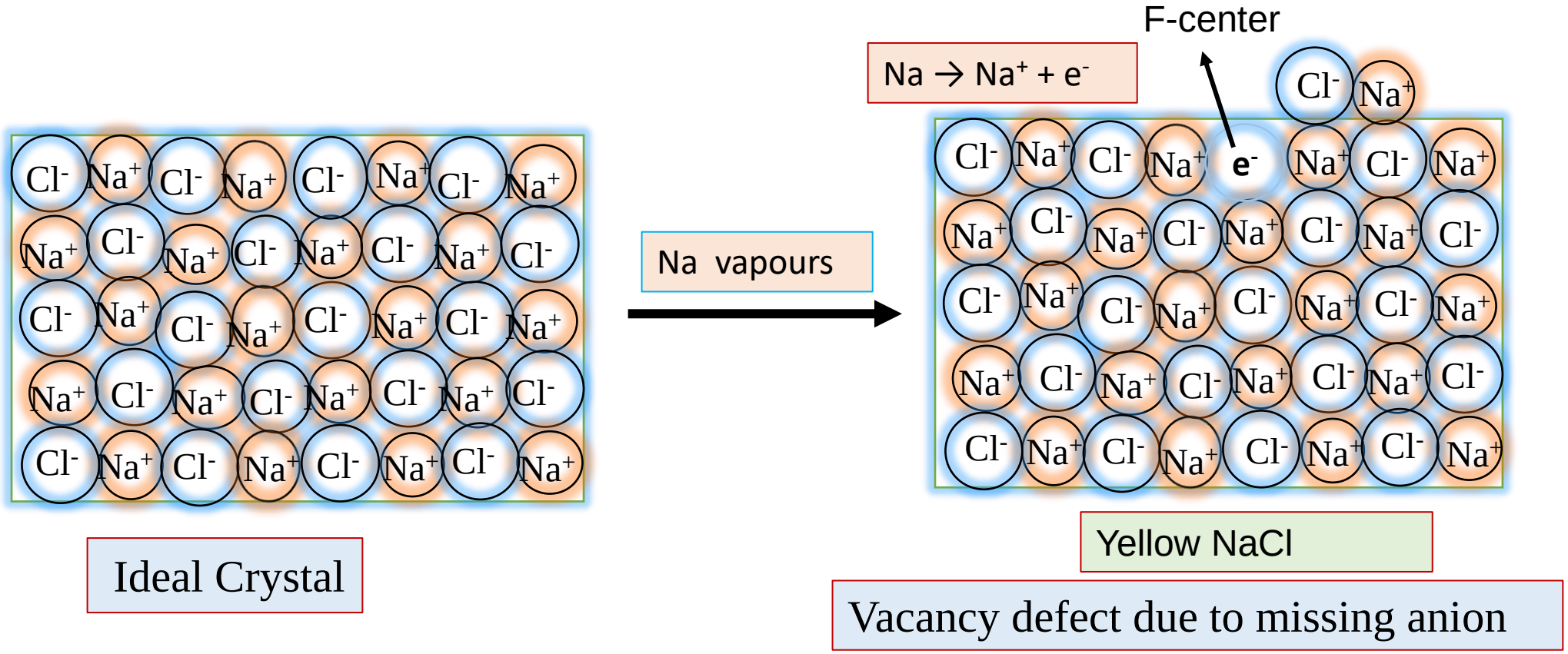
F .. Farbe means colour (German)

Defect is similar to a Schottky defect in that there are ‘holes’, but only one ‘hole’ is formed rather than a pair which is occupied by an electrons.



Thus, this types of defect is formed by crystals which would be expected to form Schottky defect

E.g. Compounds such as NaCl, KCl, LiH or δ-TiO, when heated with excess of their constituent metal vapours or treated with high energy radiation, they become deficient in the negative ions ($MX_{1-\delta}$, δ is a small fraction),



Consequences of F-centers:

- Solid can conduct electricity to small extent
- Materials with F-centers are irradiated with light they becomes photoconductors.
- Material with F-centers is n-type semiconductor, as electron in F-centers absorbs light (or heat) energy, and promoted into conduction band and since conduction is by electrons
- Solid with metal excess (F-centers) are coloured due to presence of free electrons

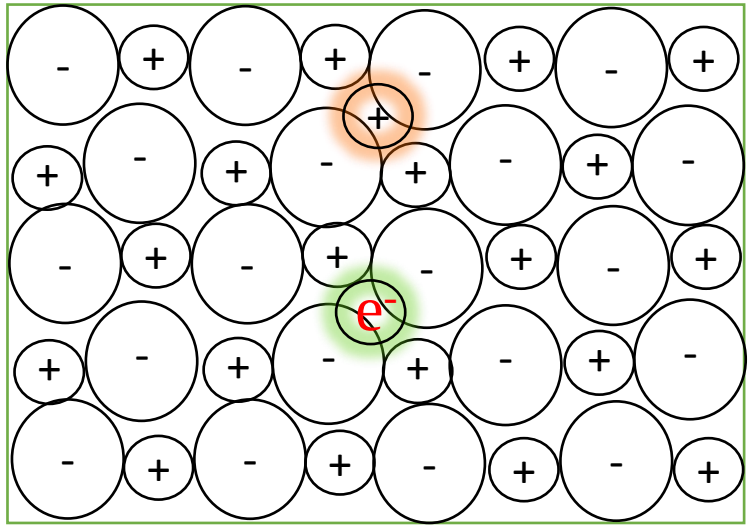
More the F-centers present, the greater the intensity of the coloration.

- Non stoichiometric NaCl is yellow while KCl is blue-lilac
- Density decreases due to absence of anionic sites.
- F-centers are paramagnetic because the electron occupying the vacant sites are unpaired.

2. Presence of extra cations in interstitial position (Interstitial ions and electrons): The extra positive ion occupies interstitial sites and electrical neutrality is maintained by the inclusion of an interstitial electron ($M_{1+\delta}X$).

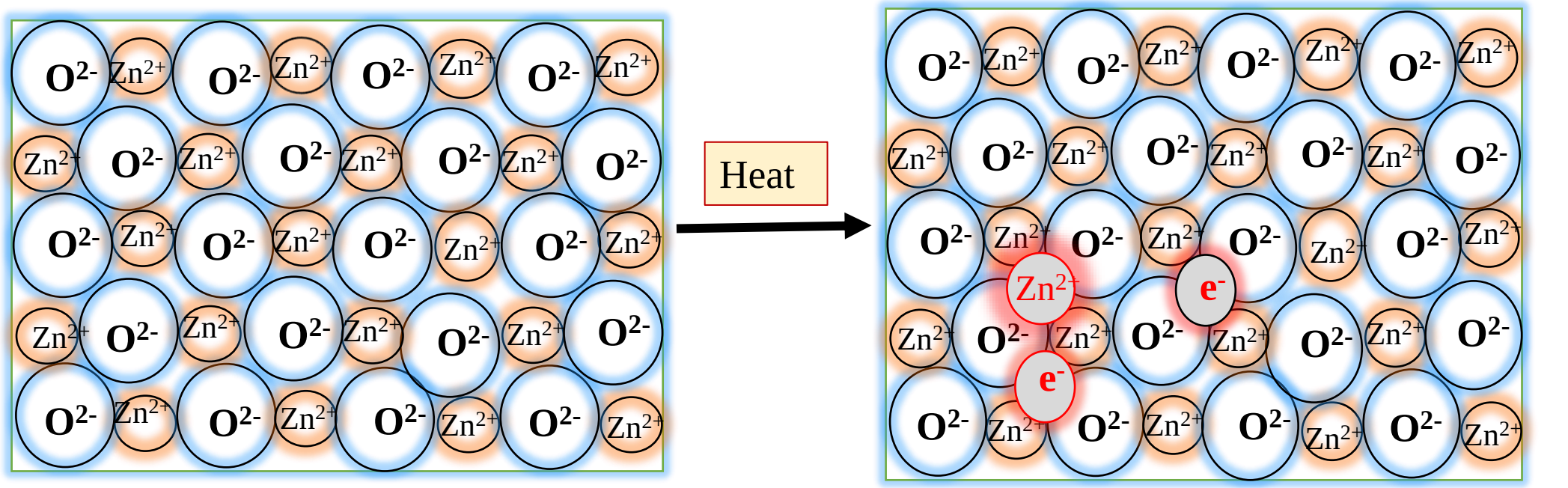
This is similar to Frenkel defect but differ in having no holes but having interstitial positive ions and electrons. E.g. CdO, Fe_2O_3 and Cr_2O_3.

Hence observed in crystals which are likely to form Frenkel defect



When, ZnO is heated, it loses oxygen reversibly at high temperature, as

$$ZnO \xrightarrow{\text{Heating}} Zn^{2+} + \tfrac{1}{2} O_2 + 2e^-$$



Consequences:

- Solid can conduct electricity to small extent
- Free electron is promoted into conduction band, and since conduction is by electrons, material is term as n-type semiconductor
- Free electrons may be excited to higher energy levels giving absorption spectra, and in consequence their compounds are coloured.

  Non stoichiometric NaCl is yellow while KCl is blue-lilac

  ZnO is white when cold but turn yellow on heating.
- Compounds are paramagnetic

Metal Deficiency Defect:

Compound may be represented by general formula $M_{1-\delta}X$.

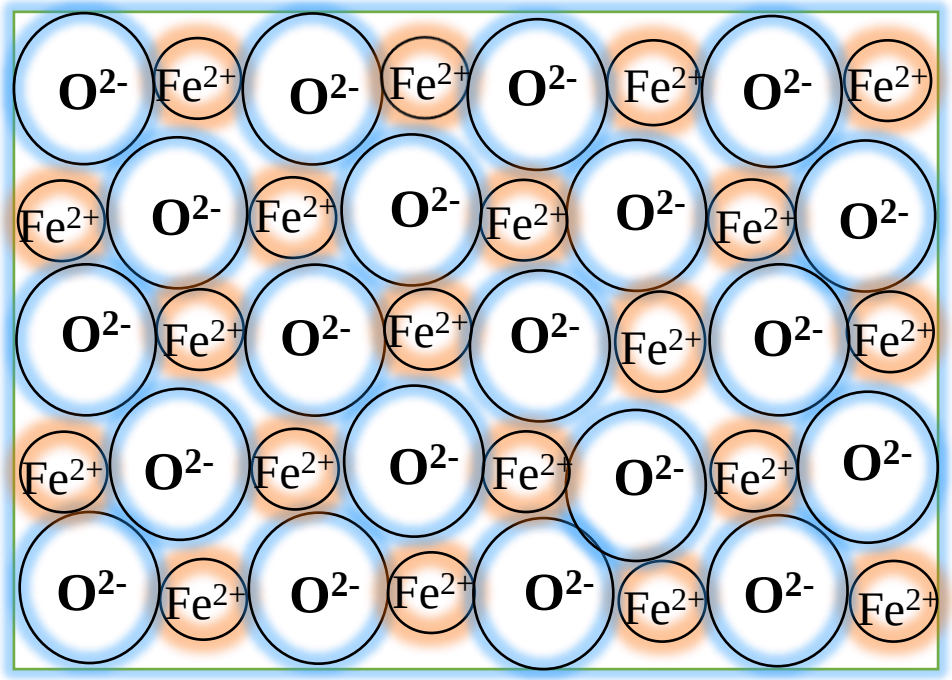
It occurs in metal which has variable valency e.g. transition metals.

They occurs in two ways:

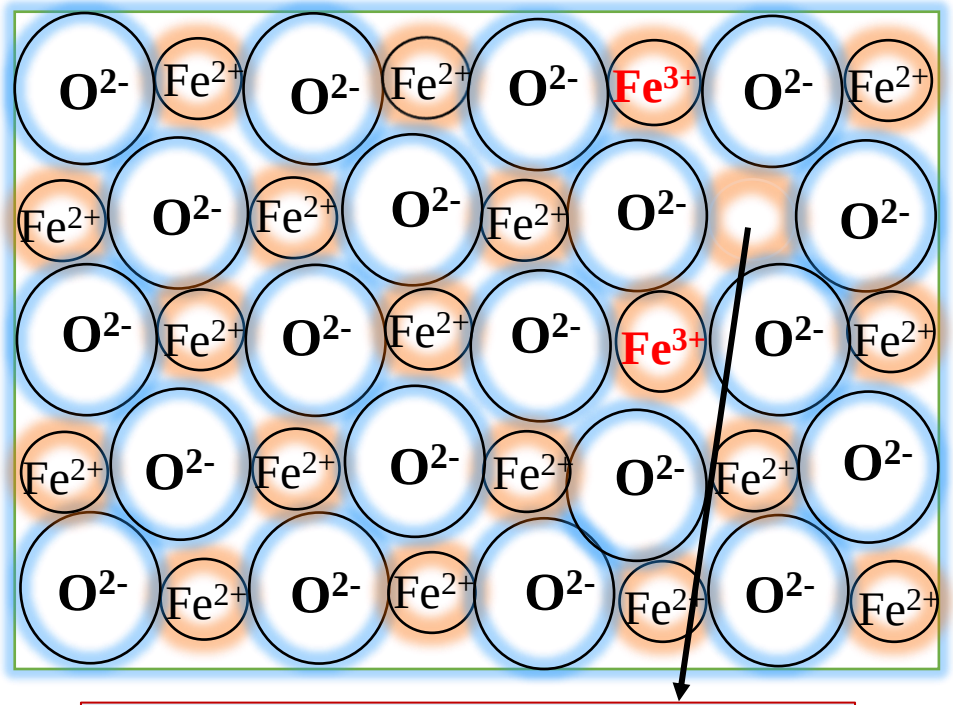
1. Positive ions absent

If a positive ion is absent from its lattice site, the charges can be balanced by adjacent metal ion having an extra positive charge.

Eg.: FeO, FeS, NiO, Cu_2S, CuI



Ideal/Perfect Crystal

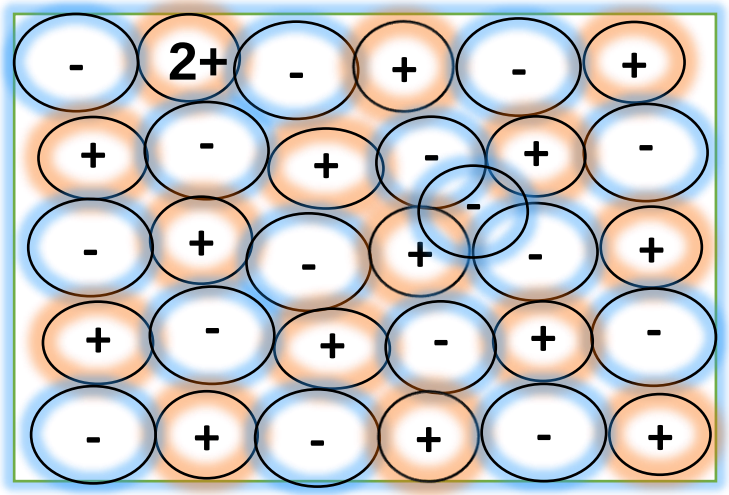


Positive ions (Fe^{2+}) absent

If a defect oxides of this type is heated in dioxygen, its room temperature conductivity increases, because the dioxygen oxidizes some of the metal ions, and this increases the number of positive holes.

2. Extra interstitial negative ions:

In principle it might be possible to have an extra negative ion in interstitial position and to balance the charges by means of an extra charge on the adjacent metal ion.



However, anions are usually large.

It would be difficult to fit them into interstitial positions.

Consequences of Metal deficiency defects:

- Solid can conduct electricity to small extent due to electron hops from an A^{+} to A^{2+} metal ions in one direction and positive holes migrates in the opposite direction across the structure, material is term as p-type semiconductor (migration of positive holes)
- Conductivity increases with increase in the number of positive centres.

References:

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Thank You